Polychlorinated Dibenzodioxins and Dibenzofurans in the Aluminium Recycling Process

Andreas Kaune[1], Karl-Werner Schramm[2], Robert Lehnardt[2], Antonius Kettrup[1,2],
Ina Ollenschläger[3] and Hartmut Rossel[3]

[1] Technische Universität München, Lehrstuhl für Ökologische Chemie und Umweltanalytik,
D–85350 Freising, Germany
[2] GSF – National Research Center for Environment and Health, Institute of Ecological
Chemistry, Ingolstädter Landstraße 1, D–85764 Neuherberg, Germany
[3] VAW aluminium AG, Entwicklungszentrum Recycling, Georg-von-Boeselager-Straße 25,
D–53117 Bonn, Germany

Introduction

After emissions of polychlorinated dibenzodioxins and dibenzofurans (PCDD/F) from waste incinerators were reduced dramatically other thermal PCDD/F sources gained in importance. Among these sources are secondary aluminium melting processes. Aluminium scrap, to which organic material is attached, is molten together with salt at temperatures of about 700 to 800 °C. These conditions are favorable for PCDD/F production. Thus, there is a need to reduce PCDD/F emissions from the aluminium recycling process by primary and secondary measures.

To meet these objectives, we performed experiments at a pilot-scale rotary furnace of the VAW aluminium AG. Compared to previous investigations on PCDD/F emissions from large-scale secondary Al plants [1,2,3], the experiments on the pilot-scale level have the following advantages: a) a single type of Al scrap can be used, b) the exhaust gas is not emitted from various furnaces that are differently operated but from a single furnace operated under well defined conditions, c) the exhaust gas from the furnace can be sampled separately from the exhaust gas of the converter while both exhaust gas streams are typically combined in large-scale plants.

Complementary to the pilot-scale experiments, formation mechanisms of PCDD/F in secondary aluminium processes were investigated under well-controlled laboratory conditions [4]. Additionally, we apply a biological toxicity test as a fast and low-cost screening method that detects total toxicity equivalents of PCDD/F and related compounds [5].

Materials and Methods

Experiments were performed at the pilot-scale furnace of the VAW aluminium AG utilizing Used Beverage Cans (UBC) as input material. This Al scrap contains large amounts of organic material (up to 4 %) and was therefore expected to produce high PCDD/F emissions. By using UBC, we expected that emission control measures would also be more evident. Please note that in large-scale plants, UBC comprise only a minor fraction of the input material or they undergo a pre-treatment before being fed into the furnace. Thus, PCDD/F emission cannot directly be transferred to large-scale plants.

The following experiments were performed: a) In the typical setup of the rotary furnace, the burner is installed at one side and the exhaust gas leaves the furnace at the opposite side. An alternative duct configuration was tested in which the exhaust gas leaves the furnace at the burner-side. b) Using the typical setup of the rotary furnace, PCDD/F emissions from pre-treated (shredded) UBC were compared to emissions from untreated UBC that were pressed to packages. c) Two different types of scrap feeding were investigated: batch-wise and continuous feeding of shredded UBC. In all these experiments, the exhaust gas was cleaned in a baghouse filter and was sampled simultaneously downstream of the rotary furnace, and upstream and downstream of the baghouse filter (Figure 1). d) Finally, post-combustion with subsequent quenching was investigated taking samples downstream of the following devices: furnace, post-combustion chamber, quenching unit, and wet scrubber (Figure 1).

Each of these experiments was done three times but sometimes only two replicates were analyzed. Each treatment was preceded and followed by a blank experiment in which only salt was fed into the furnace. In addition to the exhaust gas at up to 4 sampling points, the following matrices were sampled: input materials (aluminium scrap and salt), slag, $Ca(OH)_2$, fly ash from baghouse filter and fly ash deposited in the ducts. However, this contribution focuses on the exhaust gas samples, mainly those from the sampling point downstream of the furnace.

PCDD/F were sampled isokinetically (according to VDI 2066, Blatt 1) with a sampling train that constantly and automatically adjusts the sampling to isokinetic conditions [6]. PCDD/F were trapped in impingers filled with ethoxyethanol according to VDI 3499, Blatt 3. Analytical details and quality assurance measures of the PCDD/F analysis are described in references 7 and 8. Exhaust gas concentrations were expressed in ng per m^3 of dry air under standard conditions.

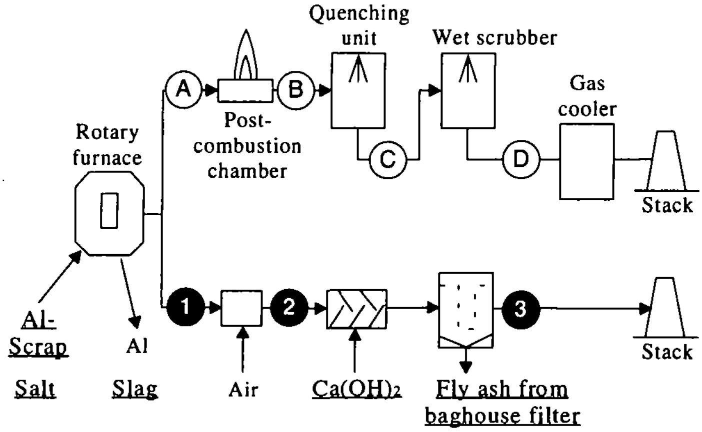

Figure 1. Schematic diagram of the pilot-scale plant and of the sampling points.

Results and Discussion

If not otherwise indicated, all results refer to the sampling point downstream of the furnace.

Duct configuration. PCDD/F emissions from the conventional duct configuration were 1.7 and 9.1 ng I-TE/m^3, those from the alternative duct configuration were 2.2 and 6.4 ng I-TE/m^3. We hypothesized that in the alternative duct configuration the exhaust gas has a longer residence time in the furnace so that a post-combustion takes place and PCDD/F emissions are reduced. Contrary to this expectation, PCDD/F were in the same range as observed for the conventional duct configuration. However, some improvements can be made in the alternative duct configuration so that there is still a chance to reduce PCDD/F emissions by this type of primary measure.

Pre-treatment of the Al scrap. The experiments described above on the different duct configurations were made with UBC that were pressed to packages. A simple pretreatment is shredding the material. This is to avoid that the packages break off irregularly and that the organic material present on the surface of the Al scrap is combusted irreproducibly. In spite of this hypothesis, PCDD/F emissions from shredded material (12 and 13 ng I-TE/m^3) were slightly higher than those of packages (4.5 and 5.6 ng I-TE/m^3, and results given above for the different duct configurations).

Different type of feeding the Al scrap. Shredded Al scrap does not have to be fed into the furnace batch-wise producing high PCDD/F emissions (12 and 13 ng I-TE/m^3). Instead of batch-wise feeding, shredded Al scrap can be fed continuously over a longer period of time. Continuous feeding reduced PCDD/F emissions to 3.5, 1.0 and 0.44 ng I-TE/m^3. This can be explained by several reasons. First, during continuous feeding the burner can also be operated continuously leading to higher temperatures and better combustion of the organic material. Second, the amount of organic material introduced into the furnace per unit of time is lower. This will also lead to better combustion and lower PCDD/F emissions. As a conclusion, continuous feeding of Al scrap is an effective primary measure to reduce PCDD/F emissions from the furnace. Furthermore, the results given in this paragraph demonstrate the high variability that may be encountered in experiments on a pilot-scale level. This makes it difficult to clearly assess the efficacy of PCDD/F reduction measures and requires that replicated experiments are performed and analyzed.

Post-combustion and quenching of the exhaust gas. The flue gas was typically cleaned in a baghouse filter that effectively removed PCDD/F (data not shown). Furthermore, post-combustion was investigated. PCDD/F found downstream of the furnace (sampling point A in Figure 1) were destroyed during post-combustion so that the I-TE level decreased from 6.4 ng I-TE/m^3 downstream of the furnace to values close to background levels after post-combustion (sampling point B) (0.00006 ng I-TE/m^3, not including non-detected congeners). During post-combustion, temperatures were about 950 °C. The exhaust gas was then quenched to 120 °C by injection of water. The aim of quenching was to quickly pass the temperature range in which PCDD/F are formed. Even with quenching, I-TE increased but the I-TE level at sampling point C was still very low (0.005 ng/m^3). In the wet scrubber, the I-TE level slightly decreased again to 0.002 ng/m^3 at sampling point D. This is partly due to the fact that PCDD/F adsorbed to particles were eliminated in the wet scrubber. Indeed, 720 ng I-TE/kg were found on the particles of the wet scrubber.

PCDD/F pattern. The homologue pattern in emission samples from the pilot-scale plant was characterized by a dominance of PCDF over PCDD (Figure 2). The fractions of the PCDF homologues decreased with increasing degree of chlorination. Among PCDD, the fractions of tetra- to hexachlorinated homologues were very similar and higher than those of the hepta- and octachlorinated PCDD. This homologue pattern was observed downstream of the furnace, but also upstream of the baghouse filter. It deviates from homologue patterns reported for other matrices from the secondary aluminium melting process [1].

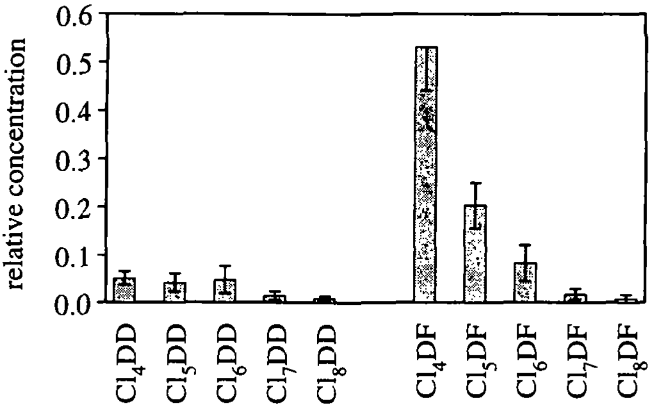

Figure 2: Mean PCDD/F homologue pattern obtained by dividing the concentration of each homologeous group by the sum of PCDD/F. Given are the mean and standard deviation of all emission samples reported in this paper (n = 9) except the emission downstream of the post-combustion chamber and those of the experiments on different duct configurations. In the latter experiments, relative Cl_4DD to Cl_6DD concentrations were slightly higher.

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